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## SOLVENT EXTRACTION OF METALS FROM LIQUID PHOTOGRAPHIC WASTE USING ACIDIC EXTRACTANTS

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**Abstract.** Currently, the exhaustion of hazardous wastes from industrial becomes a more serious problem all over the world. If we focus to photographic waste, the valuable metals and its toxicity become a factor of consideration in economic and environmental aspects for recovery and separation. Solvent extraction technology is a technique which has a great potential for metal recovery. Therefore, different types of acidic extractants (Cyanex 272, Cyanex 302, and D2EHPA) were examined in terms of their capability and selectivity in extracting metals from photographic wastes. It was found that an extractant containing a P=S functional groups (Cyanex 302) strongly extracts almost 97% silver at pH equilibrium ranging from 6 to 9. It is also found that Cyanex 302 was very selective towards silver than other metals that existed in the real photographic waste. The Cyanex 272 and D2EHPA also provide a good metal extraction performance at pH 7 and 8.3 respectively but they are only selective to iron at pH 9. Furthermore, the extraction capacity increases with increasing in extractant concentration until it achieves plateau due to excess of free extractant.

**Keywords:** Solvent extraction, acidic extractant, photographic waste, silver, Cyanex 302

**Abstrak.** Pada masa kini, pembuangan sisa berbahaya daripada industri menjadi satu masalah besar kepada dunia. Jika kita memfokus pada sisa fotografik, faktor yang dipertimbangkan ialah logam bernilai dari segi ekonomi dan ketoksikan dari aspek alam sekitar bagi tujuan perolehan semula atau pemisahan bahan tersebut. Teknologi pengekstrakan pelarut adalah salah satu teknik yang berpotensi bagi penghasilan semula logam. Dalam kajian ini, beberapa agen pengekstrak berasid (Cyanex 272, Cyanex 302, dan D2EHPA) telah diuji dari segi kemampuan dan kepemilihannya dalam mengekstrak logam daripada sisa fotografik. Hasil kajian mendapati pengekstrak yang mempunyai kumpulan fungsi P=S (Cyanex 302) telah dapat mengekstrak perak sebanyak 97% pada julat pH keseimbangan antara 6 hingga 9. Kajian juga menunjukkan Cyanex 302 memberikan kepemilihan yang baik terhadap perak berbanding logam-logam yang lain. Walau bagaimanapun Cyanex 272 dan D2EHPA juga menunjukkan pengekstrakan yang baik terhadap logam lain pada pH 7 dan pH 8.3 dan bersifat memilih hanya terhadap logam ferum pada pH 9. Selain itu kapasiti pengekstrakan bertambah dengan kepekatan pengekstrak sehinggalah lebihan pengekstrak berlaku.

**Kata kunci:** Pengekstrakan pelarut, pengekstrak berasid, sisa fotografik, perak, Cyanex 302

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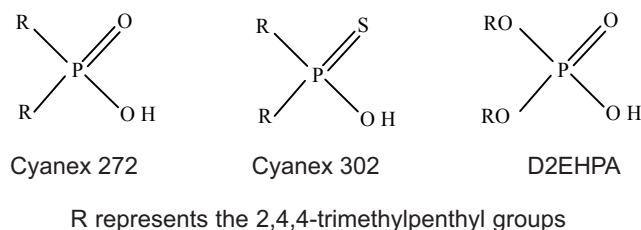
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## 1.0 INTRODUCTION

In photographic industry, recycling silver is done for development and fixing solution, spent rinse water and scrap films. These solutions are particularly interesting as the respective treatability schemes especially from economic point of view, due to the value of contained silver and their compliance with waste water discharge standards, due to silver toxicity. There are many methods which have been established commercially to recover silver that exists in photographic wastes such as precipitation, electrolysis, ion-exchange, and reductive exchange. For instance, electrolysis method is commonly used to recover silver from photographic wastes but it is not suitable for dilute silver concentration (less than 100 ppm), so that the plating efficiencies are very low. This process requires high initial capital investment and operating cost, and critical operating conditions that need to be constantly supervised. In fact the oldest and conventional method of silver recovery, precipitation, would be very difficult to achieve the discharge level although it has provided an effective technique for silver recovery. Besides, it also faces several problems because of industrial effluents containing complexing agents which might tie to the silver metal. This metal complex is sometimes very stable and cannot be precipitated by precipitation process.

Due of this property, solvent extraction process has been reported as having a great potential to recover silver from photographic wastes. This process has been extensively used in hydrometallurgical operations and more recently in the treatment of wastewaters to remove soluble metals. Since salt usually is not soluble in organic solvents, the extraction process requires the introduction of an extractant that will combine with the metal ions to form an organic soluble species. Most of the general types of compound available as extractants are dicarboxylic acids, aliphatic amines, aromatic amines, amino acids, and hydroxyl acids [1]. In general, these extractants can be categorized into three groups namely; extractant involving compound formation, ion association and solvating extractants. The extraction capacity and selectivity of extractants depend on several parameters such as extractant types and concentration, diluent, and metal ions types and concentration. In the case of metal recovery processes from a mixed metal solution such as photographic wastes, selectivity of extractant towards a target metal is important in order to obtain high purity of the recovered metals.

One group of extractants that is mostly used in silver extraction is organophosphorus compound such as bis(2-ethylhexyl) phosphoric acid (D2EHPA), bis(2,4,4-trimethylpentyl) phosphonic acid (Cyanex 272) and bis(2,4,4-trimethylpentyl) monothiophosphonic acid (Cyanex 302) (Figure 1). Sulfur substitution phosphinic acids like Cyanex 302 and Cyanex 301 are known to be employed as extractants for the extraction studies of transition metals [2]. The Cyanex 302 is the substitution of sulfur in organophosphorus acids ( $P=S$ ) that gives a different properties to the extraction molecules, as predicted by the Hard-Soft Acid-Base (HSAB) principle [3]. Most extraction studies reported in literatures [4-8] using these extractants involve



**Figure 1** Chemical structure of acidic extractants [9]

extraction of metals from pure metal solutions. There has been very little work on the evaluation of the selectivity of metal extraction from a mixed metal system such as extraction of metal from industrial wastes.

This paper presents the solvent extraction process of acidic extractants (Cyanex 302, Cyanex 272 and D2EHPA) with some accounts on selectivity of metals from liquid photographic wastes, which contain mostly of silver, sodium, potassium and iron. The effects of equilibrium pH, extractants selectivity and extractant concentration are examined.

## 2.0 EXPERIMENTAL

### 2.1 Reagents and Solutions

Cyanex 272, Cyanex 302 and D2EHPA were obtained from Fluka Company. All extractants were dissolved in kerosene as a diluent. All extractants and the diluent used are industrial grade and used as received. Nitric acid and sodium hydroxide solutions were used to adjust the initial pH of the photographic waste solutions. The photographic waste sample used was obtained from photographic shops. Since the photographic waste sample is very sensitive to temperature as well as light, it was therefore kept in a refrigerator to prevent any ageing effect or sedimentation of the sample constituents.

### 2.2 Waste Characterization

The metal contents in the photographic waste were measured using the Atomic Absorption Spectrophotometer model Philips PU9200X. The anion contents in the photographic waste samples were measured using Ion Chromatography model LC 20 with electric chemical detector model ED40. The pH measurements were carried out using pH meter model Cyberscan 100. The determination of the kinematics viscosity,  $\nu$ , was carried out by measuring the time required for a volume of liquid to flow under gravity using a calibrated glass capillary viscometer. The density ( $\rho$ ) of the photographic waste samples was measured using hydrometer.

## 2.3 Experimental Procedure

The initial pH of the photographic wastes was measured using a pH meter. The extraction process was carried out by mixing an equal volume (25 ml) of photographic waste and organic extractant solutions using a mechanical shaker at a speed of 250 rpm for 24 hours, before the phases were allowed to separate. The mixture solutions were carefully poured into a separation funnel, and after the phase separation was achieved (around 15-30 minutes), an aqueous phase was carefully separated from the organic phase. The equilibrium pH of the aqueous phase was determined by measuring using a pH meter.

The concentration of metals in the aqueous phase after extraction was measured using the Atomic Absorption Spectrophotometer (AAS). The concentration of metals extracted into an organic phase was calculated based on the mass balance principle. All experiments were carried out at ambient temperature (26°C). The same procedures were repeated for different extractants.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Waste Characterization

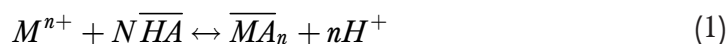
The physical and chemical characterizations of the photographic wastes were carried out in order to determine the cations and anions compositions, pH, density, and viscosity. These properties, especially those of the cations and anions compositions are important in order to explain the silver extraction from photographic waste. The cations content analyzed are silver, sodium, potassium, iron, copper, lead, chromium, cadmium, and nickel while the anions are chloride, nitrate, sulphide and fluoride. Table 1 shows that the silver, sodium, potassium, and iron exist in high concentration in the photographic wastes while the other metal concentrations are less than 1.5 ppm. The anions content are in the following order: sulphide > nitrate > chloride. However, during the photo processing, particularly in fixing or bleach-fix, silver is removed from the film or paper, usually in the form of thiosulfate complex.

**Table 1** Waste characterization of real photographic waste

Cations	Concentration (ppm)	Anions (ppm)	Concentration	Physical properties	
Ag	2490.522	Cl <sup>-</sup>	249	pH	8.02
Na	3628.63	NO <sub>3</sub> <sup>-</sup>	2202	Density	1.04 g/ml
K	6238.059	SO <sub>4</sub> <sup>2-</sup>	3712	Viscosity	0.77cP
Fe	1478.909	F <sup>-</sup>	62		

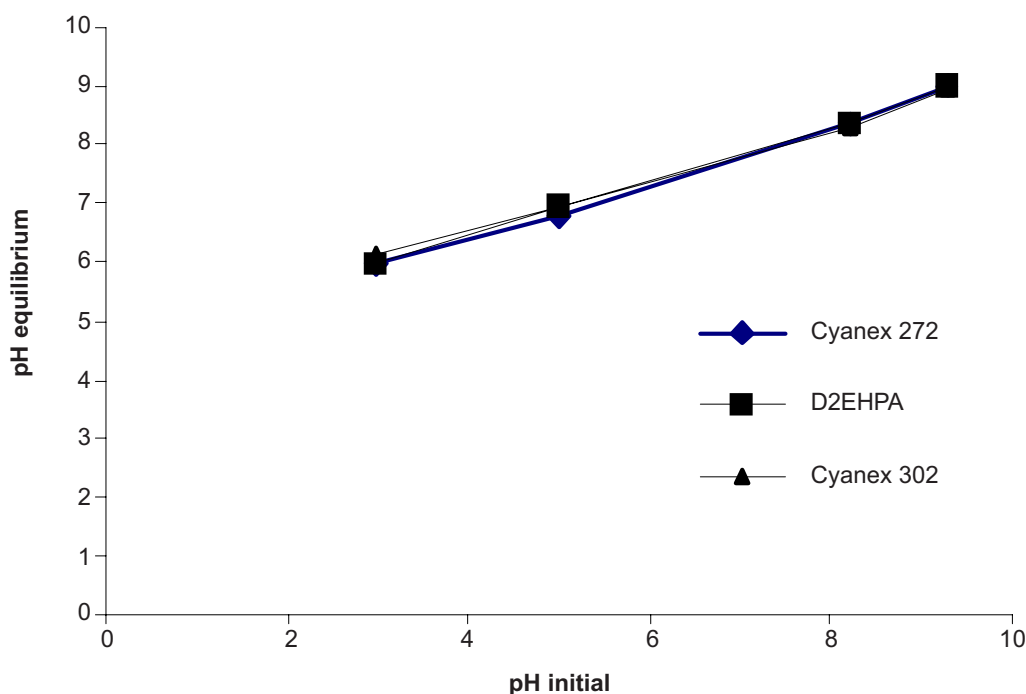
### 3.2 Effect of pH

All extractants of the acidic types used in solvent extraction processes liberate hydrogen ions during the extraction process [9]. The greater the amount of metal extracted the more hydrogen ions would be produced. These results in a decrease in pH of the system and consequently a decrease in the amount of metals extracted (the reverse reaction in Equation (1)).

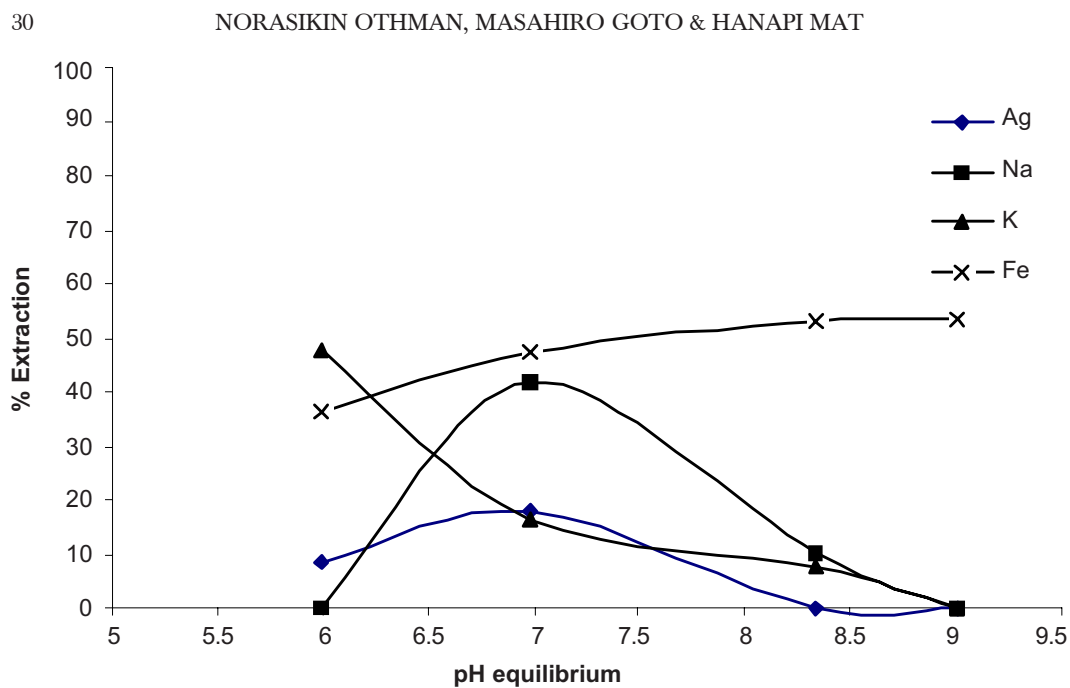


where,  $M^{n+}$  is the metal ion in the aqueous phase,  $\overline{HA}$  is the extractant,  $\overline{MA}_n$  is the metal complex compound, and  $nH^+$  is the amount of hydrogen ion released during the formation of the metal complex.

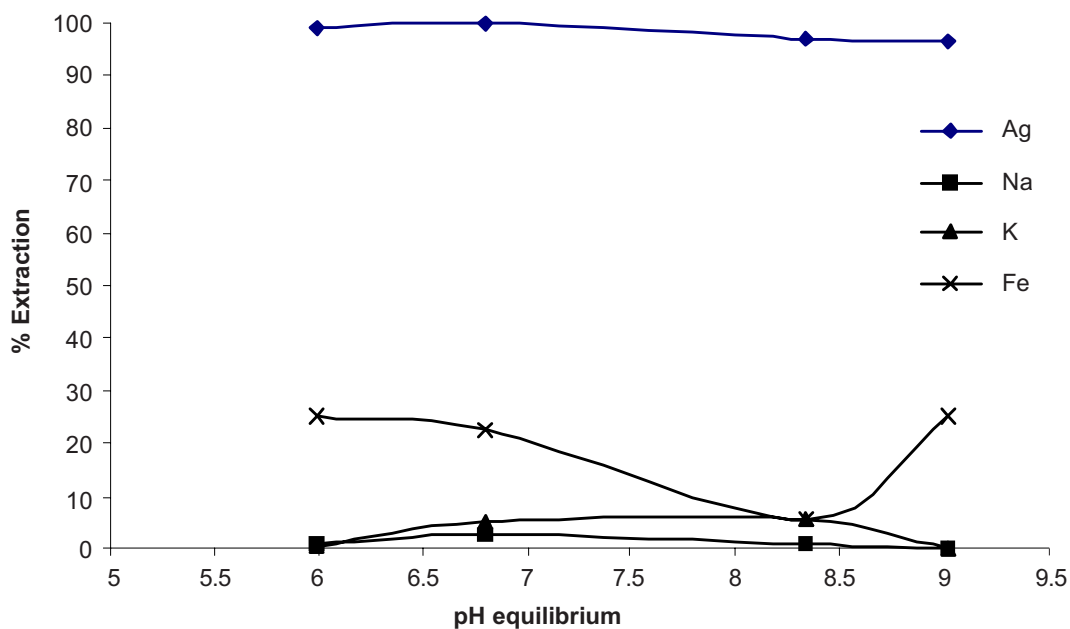
Figure 2 shows that there is no significant difference in pH equilibrium of each extractants even though the amount of metal-complexes formed depends on the types of extractant. As reported in literatures [4-8], acidic extractant is monobasic in nature and thus releases one hydrogen ion for every molecule which combines with a metal while the number of molecules of extractants involved in the formation depends on the oxidation state or coordination number of the metal ions. However, the silver extraction from photographic waste occurred at a relatively higher equilibrium pH. Throughout the extraction process, the pH of the system changes



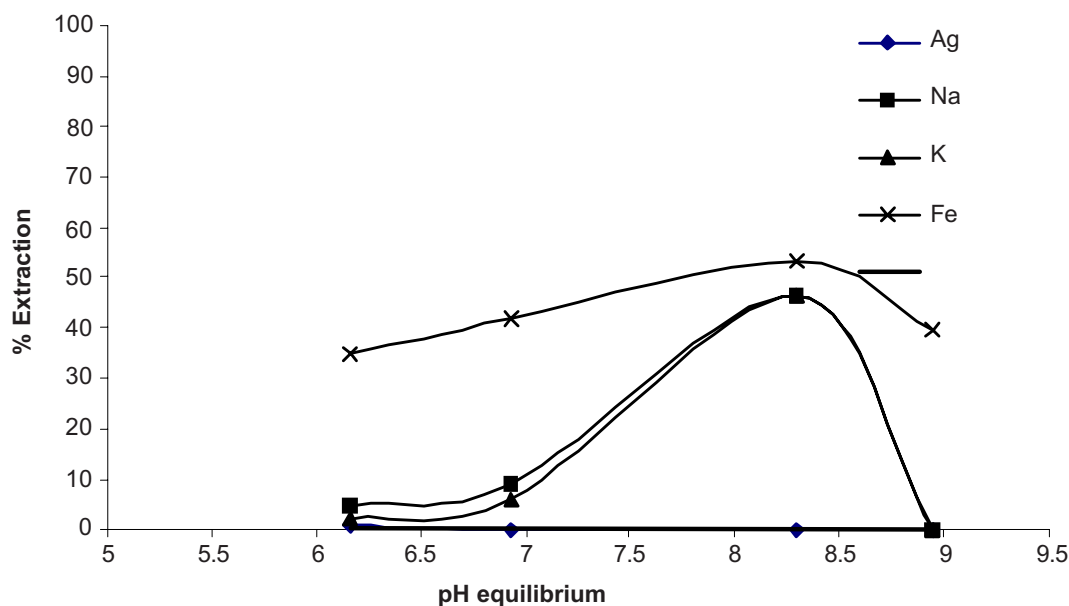
**Figure 2** Effect of pH initial on pH equilibrium



**Figure 3(a)** Metal extraction using 0.05 M Cyanex 272



**Figure 3(b)** Metal extraction using 0.05 M Cyanex 302



**Figure 3(c)** Metal extraction using 0.05M D2EHPA

continuously until it reaches the equilibrium state. This is due to the complexity of the system. During the process, some reactions in terms of association of extractant with metals will take place. This will subsequently change the environment of the system and alter the pH value. At equilibrium pH, the condition of the system is consistent and stable.

Figures 3(a-c) show the effect of equilibrium pH on metal extraction using different types of extractants in 0.05 M solutions. The percentage of metals extracted increases with equilibrium pH up to certain pH then decreases except for iron and silver in Cyanex 272 and Cyanex 302 respectively. This is due to the fact that the extractant is unable to ionize as a result of higher concentration of hydrogen ion, so that no metal complex was formed and hence extraction will not occur while at higher pH, the extraction decreases as a result of hydrolysis of metals ions [9].

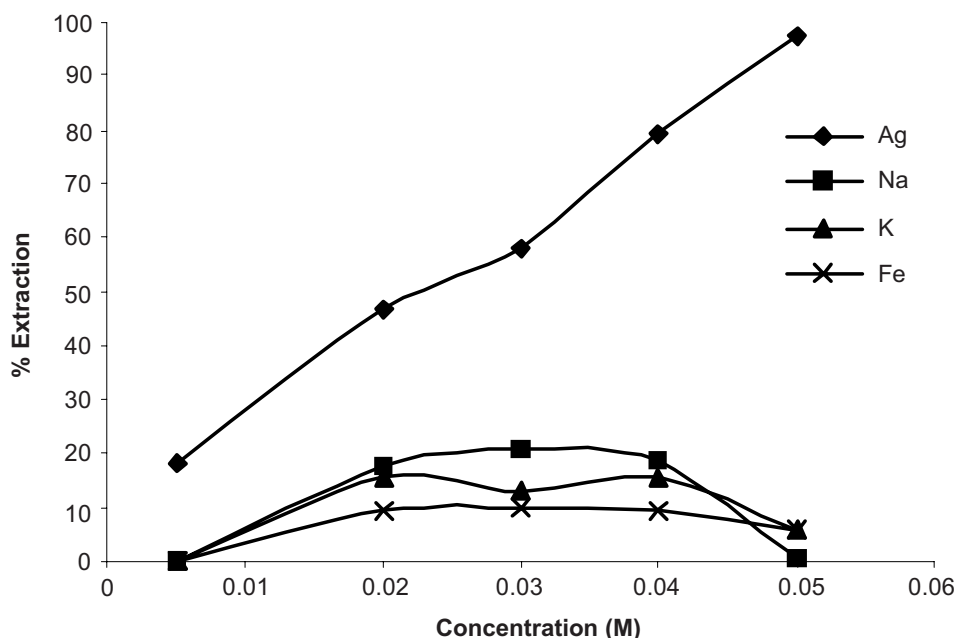
### 3.3 Extractant Selectivity

The types of extractants play an important role in solvent extraction processes especially of their capability to extract metals from aqueous phase. Referring to Figures 3(a-c), the results show that the Cyanex 302 provides a good extraction on silver at a pH range between 6 to 9. However, Cyanex 272 and D2EHPA are not able to extract silver (< 20%). Figure 3(b) shows the extraction performance of Cyanex 302. The maximum percentage of iron, sodium and potassium is less than 25% while the extraction of silver is around 97%. This means that the Cyanex 302 is selective towards silver at pH equilibrium range understudied. This might be due to the fact that the

Cyanex 302 has higher acidic properties and it is more soluble in water than the other two extractants. Sulfur substitution causes this extractant acidity to increase, making them particularly suitable for the extraction of Soft Lewis Acid metal ions such as Ag(I), Ni(II), Zn(II), Cu(I), Au(I) and platinum group metals which are in accordance with the HSAB principle [4]. Therefore, reagents containing sulfur donor atoms (Cyanex 302) are expected to be strong extractants for soft metal ions such as silver.

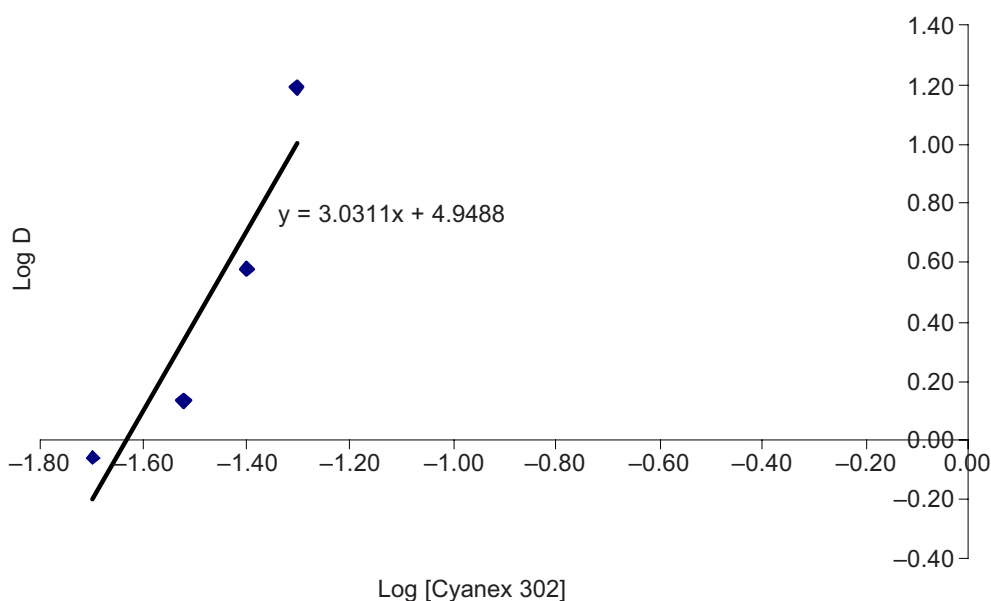
### 3.4 Effect of Extractant Concentration

Figure 4 shows the percentage of metals extraction, which increases as the extractant concentration of Cyanex 302 increased. The extraction of silver achieved 97% when using concentration of Cyanex 302 0.05 M. However, as expected at concentration higher than 0.05 M, silver extraction will plateau due to the excess of 'free' extractant. Meanwhile, the extraction percentage of other metals is almost independent of extractant concentration. It was observed that at very low extractant concentration, metal was found to precipitate due to limitation of extractant in the system in order to form metal-extractant complex that is soluble in organic phase. It was also found that the extraction of silver is very selective at 0.05 M concentration. This is due to the high potential of Cyanex 302 to form a complex compound with silver.



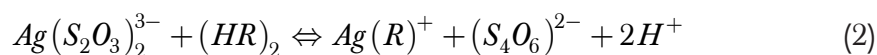
**Figure 4** Metals extraction of real photographic waste from photo shop using Cyanex 302





**Figure 5** Determination of stoichiometry of silver(I)-Cyanex 302 complex by slope ratio method

The optimum condition for the extraction of silver using Cyanex 302 was investigated by keeping the aqueous to organic phase (A/O) ratio as unity. The results obtained indicates that 0.05 M Cyanex 302 was sufficient for complete extraction of silver. The nature of the extracted species was evaluated by the plot of log D versus log[Cyanex 302], by assuming that all Cyanex 302 which exist in the system reacted with silver while percentage of other metals are negligible. The slope obtained for this plot was 3.03 (Figure 5). Hence the metal to reagent ratio was found to be 1:3.03. However, since photographic wastes is a very complicated solution containing many other types of silver ions, there is some uncertainty as to the types of extracted species which associates with Cyanex 302. Therefore, the ratio of 1:3.03 represents the combination of other types of silver ions with Cyanex 302. In the present experimental work, considering only the silver thiosulfate complex, the extraction of silver is given by the following equation:



#### 4.0 CONCLUSION

The solvent extraction of silver from a photographic waste by acidic extractants is shown to occur based on sulfur substitution in the extractant. Cyanex 302 provides a good selectivity and performance in extracting silver. The extractant concentration increases as the percentage of extraction also increase due to the existence of 'free'

extractant to form complex with metals. It was also found that from experimental observation using very low extractant concentration, the silver and other metals were observed to precipitate in the aqueous phase. However, at concentration of extractants which is higher than 0.05 M, no precipitation occurred. The Cyanex 302 provides a good extractability on silver compared to that of Cyanex 272 and D2EHPA.

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